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by

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The major research area of this program has been concerned with fundamental acts of crosslinking polymers by high energy ionizing radiation and the dependence of the crosslinking efficiency and resulting network properties on the state of the system and the temperature at the time the crosslinks are introduced. Major attention has been given to the behavior of molecular weight fractions of polyethylene, crystallized under controlled conditions and irradiated at different temperatures. A great deal of emphasis has been given to investigations directed to help in the understanding of the radiochemical acts involved in explaining the previously reported results on the relative crosslinking efficiency in the crystalline and amorphous states at elevated temperatures.

A restudy of the partitioning between sol and gel with irradiation of a very high molecular weight sample of polyethylene, $M_n \approx 7 \times 10^6$, at 133°C in the completely amorphous state substantiated the previous conclusions that the relative enhanced crosslinking in the crystalline state (at 133°C) could not be attributed to chain scission in the amorphous state. To study and analyze the radiochemical acts in more detail, the hydrogen evolution, the formation of trans-vinylene groups and the rate of vinyl decay has been studied as a function of radiation dose, temperature and molecular weight. A distinction must be made in all the measurements and analyses between the temperature and the state of the system. A new and significant result in the radiation chemistry of polyethylene has been obtained in that in the completely molten state at 133°C , where complications due to crystallinity

are absent, $G(H_2)$ is inversely dependent on the number average molecular weight. Concomitantly, the rate of vinyl decay decreases with increasing molecular weight. These new observations are self-consistent since it can be demonstrated that there is one vinyl-end group per molecule. Conventionally in the literature, the rate of vinyl decay has been taken to be a first order reaction. This conclusion is based on the study of only one unfractionated sample. Our studies as a function of molecular weight indicate, however, that the apparent first-order rate constant depends on the initial vinyl group concentration. Similar effects with molecular weight are observed in the crystalline sample at 25°C and 133°C with a significant change in the values of the parameters with temperature and phase. The above results make clear that the vinyl-end groups in both the crystalline and amorphous states act as a hydrogen "sink" and a significant amount of hydrogen initially formed is recaptured. An appropriate mechanism must therefore be developed to account for this phenomena if a theoretical material balance is to be achieved. It is clear that one needs to obtain an inherent value for $G(H_2)$ characteristic of polyethylene and independent of molecular weight (end-group effects) as a function of temperature and crystallinity. To obtain this constant for the amorphous state, studies are underway utilizing samples of very high number average molecular weight where the vinyl end-group can not be detected by infrared methods. Complications exist in determining this constant for the crystalline polymer since only the lower molecular weight samples (less than 50,000) with high initial vinyl concentrations give the very high levels of crystallinity. To circumvent this difficulty, attempts are being made to hydrogenate polyethylene, thus removing the vinyl end-group. If successful,

the samples will then be crystallized to high levels of crystallinity and the radiation chemistry studied.

The analysis of sol-gel curves of highly crystalline polyethylene, irradiated at room temperature, has indicated the distinct possibility that chain scission processes play an important role in the crystalline state as compared to irradiation processes above 90°C. Because highly crystalline polyethylene is restricted to low molecular weights the pre-gelation region is being studied by measuring the changes in intrinsic viscosity as a function of radiation dose. The data obtained to date for molecular weight fractions irradiated at different temperatures has supported the concept that the ratio of chain scission to crosslinking is substantially increased in the highly crystalline polymer at 25°C. These results are presently being analyzed in more quantitative detail and will be reported shortly.

An infrared study of linear polyethylene has been undertaken for the purposes of developing another method for establishing the level of crystallinity as well as studying segmental motions in the crystalline and amorphous regions. By preparing a wide range of molecular weight fractions of linear polyethylene crystallized in bulk under differing but controlled conditions samples having a density range from 0.99 to 0.92 at room temperature were obtained. This is by far the widest range in densities that has been studied for this polymer. It can be demonstrated that at room temperature, the gauche amorphous bands at 1352 and 1303 cm.⁻¹, the trans amorphous band at 1368 cm.⁻¹ and the trans crystalline band at 1894 cm.⁻¹ give values for the degree of crystallinity which are virtually in exact agreement with that obtained from the density. The density and infrared

absorption of these bands, for single crystals formed from dilute solution, also follow the same correlation as bulk crystallized specimens.

Studies have also been made as a function of temperature through the melting point. From studies of the higher member homologs of the n-paraffins, the specific extinction coefficients of the crystalline bands have been found to be strongly temperature dependent below their melting points. When this factor is taken into account appropriate calculations can be made, utilizing the infrared absorption, of the degree of crystallinity as a function of temperatures. Up to 100°C the degree of crystallinity remains effectively constant in agreement with thermodynamic and x-ray diffraction studies. However, above 100°C but below the thermodynamic melting range the infrared indicates an apparent partial melting. These small but detectable effects can be attributed to the motions that are starting to occur within the crystallites, as would be expected from other measurements, and is consistent with the enhanced crosslinking efficiency within the crystalline state in the vicinity of 90-100°C.

An analysis of the relative intensities of the non-crystalline bands has been made as a function of crystallite morphology and temperature. It is found by these techniques that the structure and bond orientation of the non-crystalline regions of single crystals are similar to those of the extended chain crystals formed from low molecular weight crystals, and in general can be correlated with the density. A detailed manuscript is being prepared for publication of the experimental results and analyses of the infrared studies.

A new nuclear magnetic spectrometer has been built and studies of the molecular motion as a function of molecular weight, temperature and levels of crystallinity have been initiated.